Portions of the STD Op Memo #14 have been rescinded by portions of RRD Op Memo #2. Please note the following changes to this Op Memo: STD Op Memo #14, Table 3 (Soil Leaching Methods) was rescinded by Attachment 2 of RRD Op Memo #2 ; STD Op Memo #14, Table 4 (Containers, Preservation, Holding Times) was rescinded by Attachment 4 of RRD Op Memo #2; STD Op Memo #14, Table 2 (Acceptable Analytical Methods for Common Petroleum Products) has been superceded by Attachment 1 of RRD Op Memo #2. STD Op Memo #14 Table 1 has not been rescinded.

STORAGE TANK DIVISION

SUBJECT: Analytical Parameters and Methods, Sample Handling, and Preservation for Petroleum Releases	DATE: June 12, 1998	Operational Memorandum No. 14

INTRODUCTION

This operational memorandum is intended to provide guidance to promote consistency in the selection of appropriate analytical parameters, analytical methods, sample handling, and preservation for the investigation of petroleum products released from leaking underground storage tank (LUST) sites. This operational memorandum shall apply to all new sites effective the date of this operational memorandum, and to existing sites where the field sampling has not been completed, including verification sampling.

For a more in-depth look at various petroleum product characteristics, fate and transport, sampling techniques, quality control, etc., please consult the revised Guidance for Parameters, Analytical Methods, Sample Handling, and Quality Control, for Petroleum Hydrocarbon Releases, found as Attachment No. 12, in the Guidance Document for Risk-Based Corrective Action at Leaking Underground Storage Tanks.

ANALYTICAL PARAMETERS FOR COMMON PETROLEUM PRODUCTS

Petroleum products are a complex mixture of many different components and additives. Indicator parameters or target analytes, such as benzene, toluene, ethylbenzene, and xylene (BTEX) and polynuclear aromatics (PNAs) are often used to detect the presence or absence of petroleum in environmental media. Audits conducted by Storage Tank Division (STD) staff have shown that although previous indicator parameters may be below method detection limits (MDL) or less than Tier 1 Risk-Based Screening Levels (RBSLs) in soil and/or groundwater, more persistent compounds, e.g., 1,2,4-trimethylbenzene (TMB), 1,3,5-TMB, isopropylbenzene, naphthalene and 2-methylnaphthalene remain present above their RBSLs. These components tend to be less mobile, less volatile, and less biodegradable than BTEX. In addition, some of these components are more toxic and have lower RBSLs than many of the BTEX and PNA compounds.

Many additives are commonly found in gasoline products and include octane enhancers in unleaded gasoline and anti-knock or lead scavenger additives in leaded gasoline. These additives include compounds such as methyl tertiary butyl ether (MTBE) in unleaded gasoline, and 1,2-dichloroethane (1,2-DCA), and ethylene dibromide (EDB) in leaded gasoline. The MTBE, 1,2-DCA and EDB are more mobile than BTEX and PNAs in soil and groundwater and tend to be encountered at the leading edge of the contaminant plume. The EDB and 1,2-DCA are also highly toxic carcinogens.

Based upon the aforementioned facts, it was necessary to amend the recommended parameter list, previously found in Guidance for Parameters, Analytical Methods, Sample Handling, and Quality Control, for Petroleum Hydrocarbon Releases, to include the above petroleum components to ensure proper protection of public health, safety, welfare, and the environment. Please refer to Table 1 (Recommended Parameters for Common Petroleum Products).

The recommended parameter list should be used for site characterization purposes to identify the contaminants of concern which require corrective action. Care should be taken to ensure that the more mobile groundwater contaminants are accounted for during the site characterization process. Those parameters that are not present or are below the Tier 1 Residential RBSLs may not require continued monitoring. A monitoring plan that has been submitted as part of a Corrective Action Plan (CAP) may not be changed unless an amended monitoring plan is submitted and approved by the STD project manager

Occasionally, a petroleum product (e.g., Stoddard solvents, mineral oils) will not contain indicator parameter values above the Tier 1 RBSLs, but the soil and/or groundwater impact is evident from visual or olfactory observations. In these situations, a non-specific method, such as Gasoline Range Organics (GRO) or Diesel Range Organics (DRO), may be used to evaluate the release. The GRO method is useful in evaluating petroleum solvent releases, and includes the chromatographic peaks between 2-methylpentane and 1,2,4-TMB. The DRO method is generally used for evaluating aesthetic impacts from releases of products such as fuel oil, diesel, and lubricating oils, and includes the chromatographic peaks ranging from decane to octacosane. The use of GRO or DRO method detection limits or aesthetic criteria (no visible staining or odors) are acceptable for demonstrating the site meets the unrestricted land use criteria if indicator parameters are also at or below Tier 1 RBSLs.

	Target MDL	
Method	Water	Soil
GRO	200 ug/l	5000 ug/kg
DRO	100 ug/l	4000 ug/kg

There are no numeric criteria for soil which address aesthetics. Soils which are in compliance with the appropriate health-based, chemical-specific criteria yet still exhibit adverse aesthetic impacts will have to be dealt with on a case-by-case basis. Consideration should be given to the intended use of the property, the depth of the impacted soils, the source of the contamination, and the specific adverse characteristics of the soil.

The following are general guidelines for addressing aesthetically impacted soil and groundwater at LUST Sites.

Soils:

For on-site soils with aesthetic impacts and no impacted groundwater, the owner may elect to leave the impacted soil in place as part of an unrestricted closure. If impacted soils are also located off-site, the off-site owner would have to agree to leave the impacted soil in-place. If the off-site owner does not agree that the impacted soil can be left in place, the owner or operator

who is responsible for the release is required to clean the soils up to an acceptable aesthetic criteria. Generally this criteria is the removal of soils which are visibly stained and/or soils producing an objectionable odor. In either situation, no soils which have the appearance of being saturated with product should be left in place. Any removal of soils that are aesthetically impacted must be done consistent with the provisions of Part 213, Section 21304b

Groundwater:
Where the groundwater is impacted, either on-site or off-site, the owner or operator who is responsible for the release, is required to remediate the groundwater to acceptable unrestricted aesthetic criteria or reliably restrict the groundwater for all present and future uses. Any free product present must be addressed consistent with the provisions of Part 213, Section 21307(2)(c)

ANALYTICAL METHODS

Acceptable Analytical Methods for Common Petroleum Products in groundwater and soil samples are contained in Table 2. These analytical methods should be used to evaluate contaminant concentrations for characterization and/or definition of groundwater and soil at a LUST site.

To allow for flexibility in the selection and use of different analytical methods, this list of analytical methods includes multiple methods for those cases where more than one method may be appropriate. These methods were selected based upon the need to measure contaminant concentrations at, or below, the applicable RBSLs. Please note, if there are no analytical methods capable of measuring the appropriate RBSL, the target method detection limit (TMDL) is the Tier 1 RBSL for that compound.

The Acceptable Soil Leaching Procedures for Evaluating the Mobility of Specific Contaminants in Soil can be found in Table 3. Leachate analyses can be used to help generate Site Specific Target Levels (SSTLs) and determine the potential impacts to groundwater when conducting a Tier 2 evaluation.

SAMPLE HANDLING & PRESERVATION

In order to ensure the quality of laboratory results, soil and groundwater samples must be properly collected, handled and preserved prior to laboratory analyses. Collection and handling samples in a manner that is inconsistent with the analytical testing methods may jeopardize the integrity of the sample and the validity of the sample results. Samples must be collected in a manner that minimizes the loss of organic contaminants due to volatilization or biodegradation. Please refer to Table 4 for the proper sampling handling and preservation procedures.

This memorandum is intended to provide guidance to Qualified Underground Storage Tank Consultants (QCs) and STD staff to foster consistent application of Part 213. This document is not intended to convey any rights to parties nor create or release any duties or responsibilities under the law. This document and matters addressed herein are subject to revision.

Questions concerning this operational memorandum should be addressed to the appropriate STD project manager or district supervisor responsible for the area where the site is located. In addition, any deviations from the recommended parameters shall be discussed with or justified to the appropriate STD project manager prior to making the changes.

Periodic review and revisions to this operational memorandum are the responsibility of the Chief of the Field Operations Section.

Authorization:	Date:

Distribution: Qualified Underground Storage Tank Consultants
STD Mailing List
DEQ Division/Office Chiefs
STD Supervisors

Attachments

Table 1: Recommended Parameters for Common Petroleum Products

Parameters	Leaded Gasoline[1]	Unleaded Gasoline[2]	Petro. Solv[3]	Light Distillate Oils[4]	Residual Oils[5]	Used Motor Oils[6]	Waste Oils[7]	Unknown
BTEX	X	X	X	X		X	X	X
Trimethylbenzene Isomers (TMB)[8]	X	X	X	X	X	X	X	X
MTBE		X						X
1,2-Dibromoethane (ethylene dibromide EDB)[1]	X					X	X	X
1,2-Dichloroethane[1]	X					X	X	X
PNAs[9]			X	X	X	X	X	X
Naphthalene/ 2-methylnaphthalene	X	X						X
Cadmium[10]						X	X	X
Chromium[10]						X	X	X
Lead[10]	X					X	X	X
Volatile Halocarbons[11]						X	X	X
PCBs							X	X
Diesel Range Organics (DRO)[12,13]				X	X	X	X	X
Gasoline Range Organics (GRO)[12,13]			X					X

Footnotes:

1) 1,2-dichloroethane and 1,2-dibromoethane may be present in leaded gasoline and leaded aviation gasoline and should be analyzed for if believed to be present.
2) This category includes aviation gasoline, regular, mid-grade and premium unleaded fuels or any fuel blend containing MTBE.
3) Petroleum solvents include petroleum spirits, mineral spirits, VM and P naphthas and stoddard solvent.
4) Light distillate oils include fuel oils #1, #2, diesel oils #1-D, #2-D, kerosene, Jet A and jet propellants (JP) #4, #7 and #8.

5) Residual oils include residual fuel oils #4, #5 and #6 (Bunker C), lubricating oils and hydraulic fluids. Most of these fluids are mineral oil based and can be measured by methods identified above. However, some hydraulic fluids are synthetic or water based and will not be detected by these methods.
6) Used oil is any oil that has been refined from crude or synthetic oil and as a result of use becomes unsuitable for its original purpose due to loss of original properties, or presence of impurities. Used motor oils may be suitable for further use and may be economically recyclable. Used motor oils include spent motor oils, other lubricating oils and hydraulic oils from the servicing of automotive vehicles which are not contaminated by cleaning solvents or halogenated solvents.
7) Waste oil is defined as "used oil" that has been contaminated by spilling, or by mixing with other waste, hazardous or otherwise.
8) Trimethylbenzene isomers include 1,2,4- TMB and 1,3,5- TMB.
9) PNAs includes the 16 priority pollutant PNAs listed in Method 8310 plus 2-methylnaphthalene.
10) Metals measured in water are measured as dissolved metals.
11) Measurement of volatile halocarbons in used motor oil releases is not required if there is documentation that cleaning solvents and sources of volatile halocarbons have been excluded from used motor oil.
12) GRO (Gasoline Range Organics) and DRO (Diesel Range Organics) refer to methods referenced in Measurement of Hydrocarbons: Report on Activities to Develop a manual by the EPA UST Work Group, American Petroleum Institute, Midwest Research Institute, and Enseco Incorporated.
13) The GRO and DRO methods are used to address aesthetic cleanup concerns when target analytes are not present in the soil or groundwater. These non-specific methods may be useful in evaluating petroleum solvents or aesthetic groundwater impacts arising from contaminated soils (where BETX and PNAs are absent) and stained soils and soils producing objectionable odors. At the present time, the DEQ lab is not doing GRO and DRO analyses.

Table Rescinded: See RRD OpMemo2 Attachment 1

Table 2: Acceptable Analytical Methods for Common Petroleum Products

Parameter	Water	Soil
BTEX & MTBE	8021, 8260	8021, 8260
trimethylbenzene isomers (TMB)	8021, 8260	8021, 8260
1,2-dibromoethane (ethylene dibromide - EDB)	8021, 8260	8260
1,2-dichloroethane	8021, 8260	8021, 8260
PNAs	8270, 8310	8270, 8310
naphthalene[1]	8260, 8270	8260, 8270
2-methylnaphthalene[2]	8270	8270
cadmium	6010, 6020, 7131	6010, 6020, 7131
chromium	6010, 6020, 7191	6010, 6020, 7191
lead	6010, 6020, 7421	6010, 6020, 7421
volatile halocarbons	8021, 8260	8021, 8260
PCBs	8082, 1656[3]	8082, 1656[3]
Gasoline Range Organics (GRO)	8015 Modified	8015 Modified
Diesel Range Organics (DRO)	8015 Modified	8015 Modified

Methods listed above are from EPA SW-846, **Test Methods for Evaluating Solid Waste**, unless otherwise noted. The most current version of each method listed shall be utilized.

1) Other acceptable methods, if laboratory capabilities allow, may include 8021, 8310, 8410 and 8275 (for soils)

2) Other acceptable methods, if laboratory capabilities allow, may include 8410, 8260, and 8310

3) Methods for the Determination of Nonconventional Pesticides in Municipal and Industrial Wastewater - The Determination of Organo-Halide Pesticides in Municipal and Industrial Wastewater

Other methods may be used, however they shall be preapproved by the Storage Tank Division project manager.

Implementation of Method 5035 utilizing methanol preservation for the sampling of soil volatile organic compounds, as it applies to the leaking Underground Storage Tank program, will be announced at a future date.

Table Rescinded: See RRD OpMemo2 Attachment 2

Table 3: Acceptable Soil Leaching Procedures for Evaluating the Mobility of Specific Contaminants in Soil

Leaching Procedure	Leaching Fluid	Appropriate Parameters
EPA Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) [1,2]	Buffered Acetic Acid pH: 2.88 or 4.93	Cd, Cr, Pb, PNAs, PCBs ZHE [3]: BTEX, MTBE, Method 8260 volatile organic compounds (VOCs)
EPA Method 1312 Synthetic Precipitation Leaching Procedure (SPLP) [1]	H_2SO_4 & HNO_3 @pH: 4.20 Reagent Water	Cd, Cr, Pb, PNAs, PCBs ZHE: BTEX, MTBE, Method 8260 volatile organic compounds (VOCs)
ASTM D3987-85 (ASTM Neutral) [1,4]	Reagent Water	PNAs, PCBs
ASTM D5233-92 (ASTM Single Batch) [1,2,5]	Buffered Acetic Acid pH: 2.8 or 4.93	Cd, Cr, Pb, PNAs, PCBs

Footnotes:

1) It is generally recommended, due to the spatial and temporal variations in contamination concentrations, to collect samples for both total and leachable contaminant concentrations to allow for a direct comparison between the two.
2) Sodium in the Method 1311 (TCLP) and the ASTM Single Batch extraction fluids may interfere with analysis of certain metals analyzed by graphite furnace procedures and thereby prevent attainment of the recommended method detection limits. To avoid interference from sodium, non-furnace analytical methods and/or a leachate procedure which does not contain sodium (e.g., Method 1312, SPLP) may be used.
3) ZHE: Zero Headspace Extraction is used for all volatile compounds.
4) The ASTM Neutral Leach Procedure provides for reporting the leachable contaminant levels in terms of the weight of the soil (mg/kg). However, in order to use this soil leaching procedure for the purposes of evaluating contaminant mobility and potential impact on groundwater, leachable contaminant levels must be reported in terms of the volume of the leaching fluid. This information must be conveyed to the lab prior to sample analysis.
5) This method is useful for large particle size materials. Any monolith subject to this method must also be evaluated with ASTM D4842-89 to evaluate freeze-thaw effects.

Table Rescinded: See RRD OpMemo2 Attachment 4

Table 4: Container, Preservation, and Holding Time Requirements for Common Petroleum Product Sampling and Analyses

Parameter	Matrix	Container[1]	Preservation *	Maximum Holding Time
BTEX & MTBE[7]	soil	wide mouth glass	MEOH, cool to 4°C	14 days
BTEX & MTBE[5]	water	glass	pH<2[2], cool to 4°C	14 days
Trimethylbenzene isomers (TMB)[7]	soil	wide mouth glass	MEOH, cool to 4°C	14 days (8260)
Trimethylbenzene isomers (TMB)[5]	water	glass	pH<2[2], cool to 4°C	14 days (8260)
1,2-dibromoethane (ethylene dibromide - EDB)[7]	soil	wide mouth glass	MEOH, cool to 4°C	14 days
1,2-dibromoethane (ethylene dibromide - EDB)[5]	water	glass	pH<2[2], cool to 4°C	14 days
1,2-dichloroethane[7]	soil	wide mouth glass	MEOH, cool to 4°C	14 days
1,2-dichloroethane[5]	water	glass	pH<2[2], cool to 4°C	14 days
PNAs	soil	wide mouth glass	cool to 4°C	14 days/40 days[6]
PNAs	water	amber glass	cool to 4°C	7 days/40 days[6]
Naphthalene/2-methylnaphthalene[7]	soil	wide mouth glass	MEOH, cool to 4°C	14 days/40 days[6]
Naphthalene/2-methylnaphthalene	water	amber glass	cool to 4°C	7 days/40 days[6]
Cadmium	soil	wide mouth glass	cool to 4°C	6 months
Cadmium	water	plastic or glass	HNO_3 to pH<2[3]	6 months
Chromium[4]	soil	wide mouth glass	cool to 4°C	6 months
Chromium[4]	water	plastic or glass	HNO_3 to pH<2[3]	6 months
Lead	soil	wide mouth glass	cool to 4°C	6 months
Lead	water	plastic or glass	HNO_3 to pH<2[3]	6 months
Volatile halocarbons[7]	soil	wide mouth glass	MEOH, cool to 4°C	14 days
Volatile halocarbons[5]	water	glass	pH<2[2], cool to 4°C	14 days
PCBs	soil	wide mouth glass	cool to 4°C	14 days/40 days[6]
PCBs	water	amber glass	cool to 4°C	7 days/40 days[6]
Gasoline Range Organics (GRO)	soil	wide mouth glass	cool to 4°C	14 days/40 days[6]
Gasoline Range Organics (GRO)	water	glass	pH<2[2], cool to 4°C	7 days/40 days[6]
Diesel Range Organics (DRO)	soil	wide mouth glass	cool to 4°C	14 days/40 days[6]
Diesel Range Organics (DRO)	water	glass	pH<2[2], cool to 4°C	7 days/40 days[6]

Containers, preservation and holding times are based on methods from EPA SW-846, **Test Methods for Evaluating Solid Waste**.

* Implementation of Method 5035 utilizing methanol preservation for the sampling of soil volatile organic compounds, as it applies to the Leaking Underground Storage Tank program, will be announced at a future date.

Footnotes on following page

Footnotes for Table 4:

1) Check specific method for appropriate container size. Glass screw-cap vials with Teflon lined silicone septa shall be used for liquid matrices. Wide mouth glass containers shall be capable of being hermetically sealed in the field and equipped with Teflon lined lids. Wide mouth glass containers shall be filled completely, and tapped slightly as they are filled to eliminate as much free air space as possible.
2) Adjust to pH<2 with H_2SO_4, HCl or solid $NaHSO_4$.
3) Samples for dissolved metals must be filtered immediately on site before adding preservative or lab filtered within 24 hours of collection and preserved immediately.
4) When analyzing for hexavalent chromium: aqueous samples shall be stored at 4°C±2°C and analyzed within 24 hours; soil samples shall be stored at 4°C±2°C, extracted within one month, and analyzed within four days after extraction.
5) Samples do not require acidic preservation if analyzed within seven days.
6) Aqueous samples shall be extracted within seven days and analyzed within 40 days after extraction. Soil samples shall be extracted within 14 days and analyzed within 40 days after extraction.
7) Other methods listed under Method 5035 are also acceptable.